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REMOVAL OF CU^{2+} IONS BY IMMOBILIZED A. LENTULUS FUNGAL STRAIN FROM INDUSTRIAL WASTEWATER

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ABSTRACT

In spite of applying very strict regulation for the treatment of industrial waste water because of life threatening level of the heavy metal accumulation in the aquatic life which is transferred to human bodies through food chain. For this purpose there was development of new technology in which A.lentulus strain immobilized with biopolymeric bead of alginate and gelatin was prepared and characterized by Dispersion microscope .Uptake of metal was very fast initially and equilibrium was attained within 240 min. Sorption data conformed well to Langmuir and Freundlich isotherm model. Highest Cu (II) by selected biomass (4.0 g/l, dry wt).immobilized in sodium alginate and gelatin occurred at 35 ºC, 180 rpm when initial copper concentration was 100 mg/l.

KEYWORDS: Biosorption, Metal Removal, Gelatin & Alginate Bead, A. Lentulus

INTRODUCTION

Over the past several years, the increasing contamination in various in various environmental segments due to unscrupulous discharge of trace metals from several sources is a matter of serious concern (Zuane.J.L, 1999, Bai R. S, 2003).Environmental significance of trace metals is assessed in terms of toxicity as well as the extent of their exploitations, application and consequent mobilizations into the air, water and land. These trace metals are called heavy metals providing connotation of toxicity. Various heavy metals such as cadmium, zinc, lead, copper iron, nickel and cobalt enter the environment through industrial wastes, mill tailings and landfill run off (Zuane.J.L1996, Aksu.Z, 2005, Aksu.Z, 1998)**.** Exposure of heavy metal contamination has been found to cause kidney damage, liver damage and anemia in low doses, and in high concentrations, they can be carcinogenic and teratogenic if not fatal (Vole sky B, 1990, Lin.S, 2000, Parab.H 2006)**.** The environmental Protection Agency has regulated industrial waste disposal; however, when industrial waste discharge exceed the regulated disposal amounts, many industries respond by diluting the hazardous substances are released into the environment, they naturally concentrate in wetlands and soils.

The natural process of transportation of metal ions between the soil and water consolidate heavy metal contamination in high concentrations that affect the natural ecosystem (Gale. N.L,1979).Because of increasing environmental concern regarding heavy metal contaminations, there has been an abundance of interest in the removal of heavy metal ions from contaminated soils and waste streams(Nakajima.A, 1982, Darnell. D.W, 1986, Christs R.H 1986). Although cleanup is necessary to prevent any further discharge of contaminated wastes into the environment, a technology needs to be developed that is cost- effective for industry to use. As a cost – effective alternative method, the biosorption has been emerged as an economic method both for the metal removal as well as metal preconcentration for analysis. Biosorption uses biomass raw materials which are either abundant fungi or algae or waste from industrial operations. (McHale A.P 1994,Volesky.B. 1995, Trujillo.E.M, 1995). Biosorption is a property of certain type of inactive, dead,

microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solution.

Ionic copper is far more toxic toward aquatic organism than organically – bound copper, and is more stable the copper complex, the lower the toxicity. Through the dissolved metal is the form which is toxic towards fish, the ingested particles are also rapidly absorbed from the stomach fluids to increase significantly the body burden of heavy metals in fish. Sediments may be more important than water as sources of heavy metals for bottom feeding aquatic organisms. Therefore, knowledge of chemical forms of dissolved metals is important to comprehend the heavy metal toxicity to aquatic lives and also for efficient operation of water treatment plants. The efficiency of treatment plant often depends on whether a metal is in ionic, complexes, colloidal or particulate form.

In this study, adsorption ability of immobilized A. lentulus was investigated for the removal of Cu (II) from wastewater.

METHODS AND MATERIALS

Biomass Isolation

Industrial effluents contaminated with Cu^{2+} were collected from tannery industry and textile industry from industrial area Banmore located in Gwalior, India. Both the effluents were kept at 4°C during storage and characterized. To isolate, potato dextrose agar plates for fungus were prepared and the plates were incubated at 30°C. For the fungus, monitoring was done after 96 h. The fungus colonies that appeared on Cu^{2+} amended plates were isolate, purified and characterized based on their morphological characteristics such as colour, texture, size. Further, microscopic characterization was also done. The fungal strain was identified as Aspergillus sp. Based on further characterization isolated fungal strain identifies as A. lentulus.

Biomass Preparations

Organism

A strain A.lentulus immobilized in sodium alginate and gelatin was used for biosorption of Cu (II)

Ions from aqueous solution. It was maintained by monthly sub culturing using potato dextrose agar and stored at 4ºc.

Resting Biomass

Fungal strain was grown in 250 ml Erlenmeyer flasks containing 100 ml of growth media. After exponential phase of growth, cells were harvested by centrifugation at 4000 rpm and 6 °C for 10 min. The harvested cells were washed by double distilled water. This biomass was termed as resting biomass.

Autoclaved Biomass

Autoclaved biomass was prepared by autoclaving the pre grown resting biomass at 121°C and 15 lb for 20 minutes. The autoclaved biomass was then used after filtration.

Immobilization of Biomass

A. lentulus was immobilized by mixing sodium alginate, gelatin with above resting biomass in the ratio of 1:1:5 .This mixtures were dropped in the form of beads of sodium alginate, gelatin covering the biomass. These beads were dipped into calcium chloride solution overnight. Finally beads of calcium alginate, gelatin entrapping the fungal biomass were obtained.

ESTIMATION OF COPPER

Concentration of Cu (II) in solution was estimated using Atomic Absorbance Spectrophotometer.

Copper Removal Studies Using Synthetic Solution

A weigh amount of treated/ untreated fungal biomass (4 g/l) was added in an Erlenmeyer flask containing solution of different concentration of Cu^{2+} at fixed pH and biomass dose. The effect of parameter like contact time and various different concentration of Cu^{2+} ranging from 50- 400 mg/l on Cu^{2+} biosorption was studied. The concentration of Cu^{2+} verses time was examined at various initial Cu^{2+} concentrations, for each type of biomass.

Biosorption Isotherm

Langmuir model (Langmuir I, 1916). [$q_e = q_m b.C_e / (1+b.C_e)$] may be rearranged as

$$C_e / q_e = 1/b.q_m + C_e/q_m \quad (1)$$

Where C_e is equilibrium concentration (mg/l) and q_e is adsorbed amount ion per g of biomass at equilibrium (mg/l). q_m is maximum amount of metal ion per unit weight of biomass to form a complete monolayer on the surface bound at high C_e (mg/l). b is a constant related to affinity of binding sites (1/mg). A plot of $C_e / _{vs}. C_e$ should indicate a straight line of slope $1/q_{m\ and}$ intercept of $1/bq_m$. Freundlich model equation (Freundlich H.M.F, 1906). ($q_e = k.Ce^{1/n}$) is conveniently used in linear form as

$$\text{In } q_e = \text{In } k + (1/n) \text{ In } C_e \quad (2)$$

Where K and n are Freundlich constants characteristics of the system. K is relative indicator of adsorption capacity (1/g) and n indicates intensity of adsorption.

Kinetic Modeling

First – order rate expression based on the solid capacity is generally expressed as

$$- \log 10 \, (qe - qt) \, qe = k1/2.3 \quad (3)$$

Where k1 is rate constant of First order biosorption (min -1)

Pseudo second order equation is also based on sorption capacity of solid phase (Aksu.Z, 2001, Chatterjee, 2008) as

$$1/ (qe - qt) = 1/q \, k_2 \, t \quad (4)$$

$$t / q_t = 1/h + (1 / q_t) \, t \quad (5)$$

Where $h = k_2 . qe_2$ can be regarded as initial sorption rate as $t \rightarrow 0$.If pseudo second order kinetics is applicable, plot of t/ q versus t gives a linear relationship, which allows computation of qe, k_2 values.

DESORPTION OF METAL FROM BIOSORBED CELL

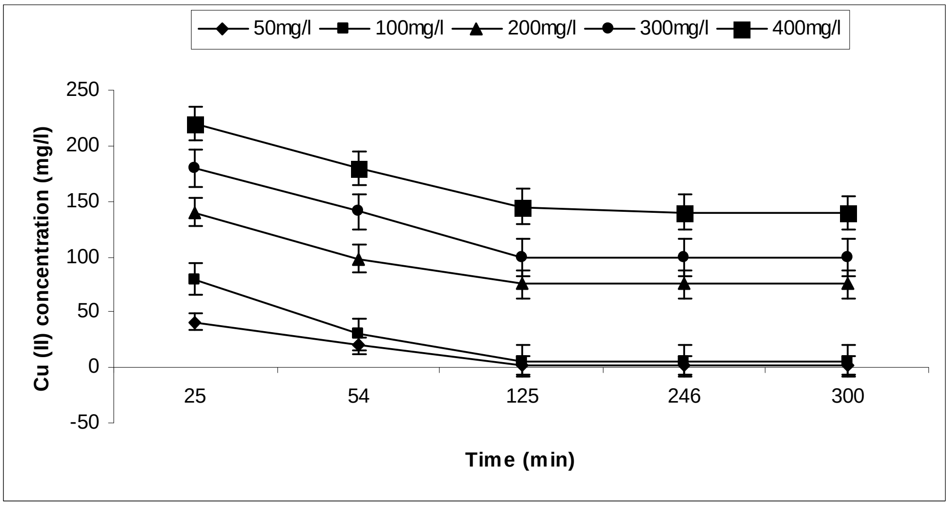
Efficiency of various eluents (0.1 M) like HCl, HNO_3, H_2SO_4, CH_3COOH and HCOOH was examined to recover copper from biosorbed fungal cells of selected strain at 35ºC and 180 rpm. To investigate desorption efficiency of different eluents, metal laden immobilized cells were filtered and after soaking in filter paper to remove any liquid adhered, these beads were transferred to 50 ml of elute taken in 250 ml Erlenmeyer flask. Each flask containing solution was incubated for 4h at 35ºC and 180 rpm. It was then centrifuged and supernatant was collected. Desorption capacity is defined as

(concentration of desorbed copper/ concentration of adsorbed copper) x 100%.

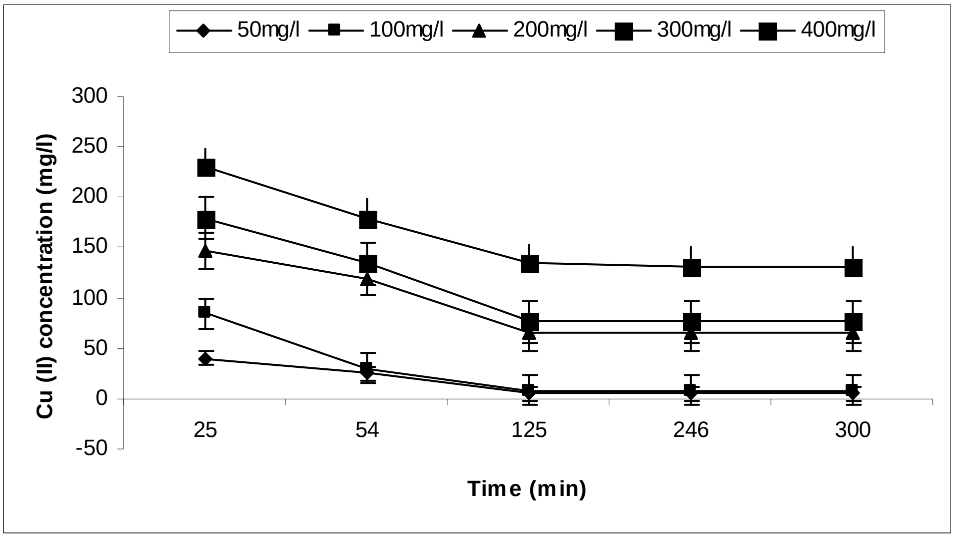
RESULTS AND DISCUSSIONS

Effect of Initial CU (II) Ion Concentration

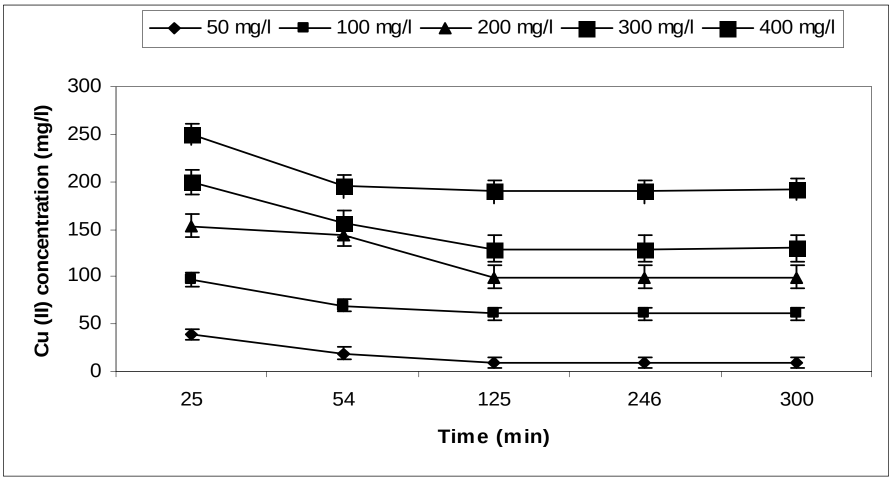
Biosorption carried out with different initial Cu (II) ion concentration (50,100,200,300,400 mg/l) was optimum at biomass concentration (dry wt) of 4.0g/l at pH= 6 with increase in initial concentration of Cu (II) ion, specific uptake increased, may be due to an increase in electrostatic interactions involving sites of progressively lower affinity for metal ions, but metal removal decreased Fig – 1.As the concentration of Cu (II) was increased from 50- 100 mg/l the percentage removal increased but it decreased when Cu (II) concentration increase from 100- 400 mg/l. The equilibrium time for resting, autoclave killed and immobilized biomass remains unaffected. by the concentration.



a] Autoclaved Biomass



b] Resting Biomass



c] Immobilized Biomass

Figure 1: Effect of Concentration of Copper Biosorption using a] Autoclaved Biomass b] Resting Biomass c] Immobilized Biomass of A.lentulus at pH-6 and Biomass dose 4.0g/l

Time Course of Biosorption

Immobilized beads containing 4.0g/l biomass in sodium alginate and gelatin matrices respectively were taken in 100 ml solution containing 100mg/l Cu (II) ion (pH=6) in 250 ml Erlenmeyer flask and incubated at 35 °C and 180 rpm for 300 min. Biosorption of Cu (II) ion was rapid and occurred during first 50 min of sorption but thereafter equilibrium was reached at 240 min.

Adsorption Equilibrium Isotherm

Freundlich (Fig-2 & Table -1) & Langmuir (Fig-3, Table– 2) models exhibited good fit to Cu (II) sorption at solution pH= 6.

Kinetics of Adsorption

Kinetics was studied with an adsorbent of entrapped in sodium alginate and gelatin at 35 °C at different time intervals up to 300 min. First order equation was applicable to all sorption data entrapped biomass with correlation co-efficient 0.9606 and 0.9991. Values of Q_m and k obtained by linear regression were 27.02 mg/g dry cell, 0.30119 g/ mg/min.

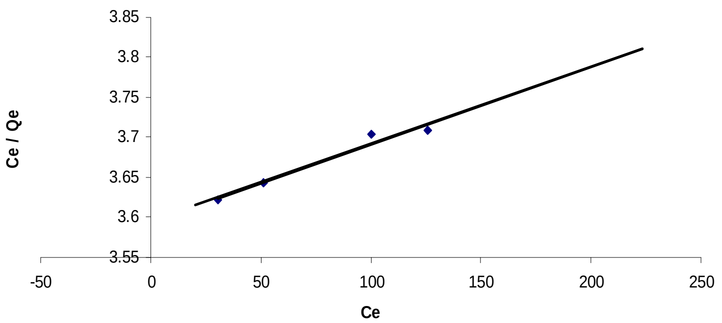


Figure 2: Langmuir Isotherm for Biosorption of Cu (II) by Immobilized A. lentulus

Table 1: Langmuir Isotherm Parameters for Cu (II) Biosorption on Immobilized A. lentulus

Q_m, mg/g Dry Weight	b, l/mg	R^2
27.02	8.53×10^{-3}	0.9606

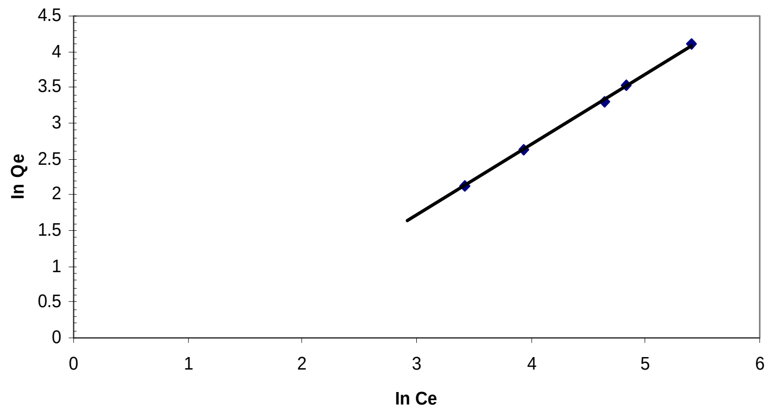


Figure 3: Freundlich Isotherm for Adsorption of Cu (II) by Immobilized A. lentulus

Table 2: Freundlich Isotherm Parameters for Cu (II) Biosorption on Immobilized A. lentulus

K	1/n	R_2
0.30119	0.9970	0.9991

Desorption Efficiency of Different Eluents

Among eluents (0.1 M each; HCl, HNO_3, H_2SO_4, CH_3COOH and HCOOH) tested to recover copper from biosorbent immobilized fungal cells of selected strain at 35oc and 180 rpm, mineral acid may act as better desolving agents than organic acids **(**Fig- 4). HCl showed maximum desorption from biosorbend cells immobilized (Chatterjee A., *2008).*

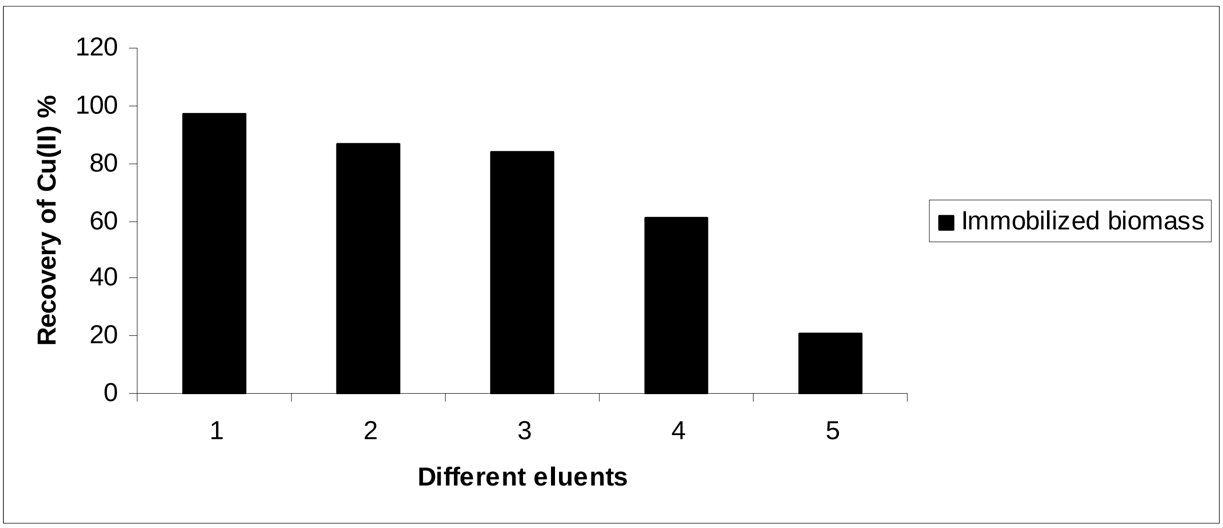


Figure 4: Desorption Capacity of Various Eluents (HCl -1; HNO_3-2, H_2SO_4 -3; CH_3COOH -4, HCOOH -5) Incubated at 35 °C, 180 rpm for 4h

CONCLUSIONS

Fungal strain immobilized in gelatin and sodium alginate was found most effective in removing Cu (II) ion from solution. Uptake of metal was very fast initially and equilibrium was attained within 240 min. Overall biosorption process was best fitted in Langmuir and Freundlich model. Highest uptake of Cu (II) 96.9% by selected biomass (4.0g/l, dry wt) immobilized in gelatin and sodium alginate occurred at 35 oC, 180 rpm when initial copper concentration was 100 mg/l.

REFERENCES

1. Zuane J. L. and kiff, R J. (1999) Hand book of drinking water quality, (Van Nostrand Reinland, New York) 2nd Edition**.**
2. R Sudha Bai, T.Emilia Abraham. (2003). Studies on chromium (VI) adsorption–desorption using immobilized fungal biomass.87 (1), 17-26
3. Zuane, J L. & Kiff, R J. (1996). Hand book of drinking water quality, 2nd Ed (Van Nostrand Reinland, New York).
4. Aksu Z., (2005). Application of biosorption for the removal of organic pollutants: a review, *Process Biochem*, 40: 997- 1026
5. Aksu Z. (1998) , A Comparative study of copper(II) biosorption on Ca - alginate, agarose and immobilized C. Vulgaris in a packed -bed column**,**Egreli G.; Kutsol T., , *Process Biochem*, 33 :393-400
6. Vole sky. B., (1990), Biosorption of Heavy Metals, CRC Press, Boca Raton, Florida, and pp. 396.
7. Lin S, H., Lai S H., Leu H, G., (2000).Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process. *Journal of Hazardous Materials,* B76, 139 – 153**.**
8. Parab H., Joshi S., Shenoys N., Lali A., (2006) Sarma U.S. Sudersanan, M, Determination of kinetic and equilibrium parameters of the batch sorption of Co(II), Cr(III) and Ni(II) onto coir pith *Process Biochemistry,* 41, 609 – 615
9. Gale N L. and Wixson B.G.., Dev., (1979) Removal of heavy metal from industrial effluents by algae. Ind. Microbial. 20, 259).
10. Nakajima A., T. Horikoshi T., Sakaguchi T., Eur. J. *(1982)* Recovery of uranium by immobilized microorganisms. *Appl. Microbiol. Biotechnol*. 16, 88.
11. K.A. Natarajan, S. Subramanian, J.M. (1999) Modak.Biosorption of heavy metal ions from aqueous and cyanide solutions using fungal biomass. Process Metallurgy.9, 351-361.
12. Christs R. H., K. Oberholeser D., Schwartz J., Marzoff and Ryder D., (1988) INTRODUCTION Algae cells and other microorganisms are capable of ad- sorbing different metalsfrom a variety of solution environments. Environ. Sci. Technol**,** 22 (7), 755.
13. McHale A P & McHale S, (1994) Microbial biosorption of metals: Potential in the treatment of metal pollution *Biotechnol Advances* 12, 647 – 652.
14. Volesky B., (1995) Holan Z.R., Biosorption of heavy metals, *Biotechnol Prog*, 11, 235-250.

15. Trujillo E M., Sprinti & Zhung H., (1995) Immobilized biomass: a new class of heavy metal bioexchangers, in Ion exchange Technol: Advances in pollution Control, edited by A K Sengupta (Technonic Publishing Company Inc., PA) 225 – 271

16. Langmuir I., (1916) *J AM Chem. Soc*, 38 2221 – 2225.

17. Freundlich H M F., (1906) Uber die adsorption in lasungen, *J Phys Chem.*, 57 385-470.

18. Ho S and McKay, G.., (1999A) Comparative sorption kinetic studies of dye and aromatic compounds onto fly ash*J Environ Sci Health*, 34 1179 – 1204.

19. Aksu Z., (2001) Equilibrium. Kinetic modeling of cadmium (II) biosorption by C. vulgaris in a batch system: effect of temperature. *Sep Puri Technol*, 21 285- 294.

20. Chatterjee A., Ray, L*l, (2008)* Biosorption of Cu (II) by immobilized biomass of Bacillus cereus M from aqueous solution *Research* 67, PP. 629-634.Edited By R. Amils and A. Ballester